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PRODUCTION OF NITROGUANIDINE WITH HIGH BULK-DENSITY¹

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Abstract

Commercial nitroguanidine will not form pourable slurries in greater than 5 to 10% concentration because of unfavourable crystal shape. Controlled crystallization from water-methanol improves this crystal shape so that slurries containing equal parts of solid and vehicle can be poured.

Nitroguanidine is an explosive of power and detonation rate approximating that of T.N.T., while its extreme insensitiveness to impact and its higher true density (1.77) offer certain advantages over the commoner military explosive. Unfortunately these advantages have not heretofore been fully realizable. The production of nitroguanidine involves a final water crystallization from which the compound appears as finely felted needles of bulk-density less than 0.3.

The fineness and crystal shape of such nitroguanidine seriously limits the usefulness of this explosive. Firstly the low weight per unit volume presents a shipping and storing problem. Even when the explosive is packaged under pressure, the contents weighs less than one-third that of a comparable box of T.N.T. Secondly, although the rate of detonation of nitroguanidine is greater than that of T.N.T. at density 1.0 (5360 vs. 4870 m. per sec.), such highly compressed nitroguanidine is not easy to produce, whereas ordinary T.N.T. can be packed by hand to this density. The brisance, or shattering effect, of an explosive is dependent on its rate of detonation, which is, in turn, directly proportional to its packed density. In practical use, therefore, the hand-packed nitroguanidine at a density of about 0.3 has a rate of detonation not greater than 3000 m. per sec. This low rate not only limits its usefulness as a brisant high explosive but also tends toward incomplete detonation (with this type of explosive) unless the confinement is extreme.

A third disadvantage of the ordinary nitroguanidine arises because of the crystal shape. The interlocking tendency of the fine needles precludes the use of the explosive in a slurry which might be used for pouring into shell,

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bombs, or other containers, unless the percentage in the slurry does not exceed an ineffective 5 to 10% of nitroguanidine.

We have found that the shape and size of the nitroguanidine crystal can be altered by crystallization from non-aqueous media to make it satisfactory in pourable slurries containing as much as 50% of the solid in liquid T.N.T. Thus, material of bulk-density 0.80 to 0.87 can be obtained by Soxhlet-extraction with hot solvent. Figs. 1, 2, and 3 are photomicrographic records of nitroguanidine crystallized from acetone, ethanol, and methanol, respectively. The crystals all had a refractive index of 1.526, identical with that of commercial nitroguanidine, and were mounted and photographed in a medium of refractive index 1.694 by Dr. W. C. McCrone of Cornell University. These 20-fold magnifications may be compared with the 100-fold magnification of a commercial nitroguanidine shown in Fig. 4 to show why the massive forms obtained from the non-aqueous solvents are more easily handled in bulk or in slurries than the felted needles produced from water. The extreme insolubility of nitroguanidine in these non-aqueous solvents does, however, make the extraction process so slow that it could have no practical importance. For the same reason a method involving alternate heating and cooling of a circulating slurry in these solvents was likewise unsuccessful.

What appears on the other hand to be a completely workable method of producing massive crystals involves the introduction of a hot saturated aqueous solution of nitroguanidine into methanol. Material with bulk-density as high as 0.96 has been produced in this manner in 90% yield per pass. The remainder of the nitroguanidine is not lost, since the methanol can be stripped from the mother liquor in a suitable still, to leave a hot aqueous residue which has been used for solution of a subsequent charge of crude nitroguanidine. One may expect that the quality of product will not be lowered by repeated re-use of the mother liquor, since evaporation of a portion to dryness gave a quantitative recovery of good nitroguanidine (m.p. 236° to 240° C.).

The superiority of this method over that of crystallization from water alone evidently depends on slow deposition over an appreciable temperature range from a dilute solution. These conditions are difficult to attain in water alone. Although nitroguanidine is much more soluble in water at the boiling point (1 part/11 parts water) than at 20° C. (1 part/375 parts of water) the greater part of this differential exists in the relatively narrow temperature range of 90° to 100° C. Indeed the rapidity with which crystallization of a saturated solution occurs in the range 96° to 100° C. caused us to decrease our initial concentration in boiling water to 1 part of nitroguanidine per 13 parts of water in order to prevent pipe-stoppage under conditions where the temperature of the conduit might drop several degrees.

The ideal medium for crystal growth is a water-methanol mixture varying from 1:2 to 1:1 parts by volume at a temperature close to the boiling point of pure methanol. This can be attained by rapid addition of the hot aqueous solution to pure methanol, initially at room temperature. A more gradual

PLATE I

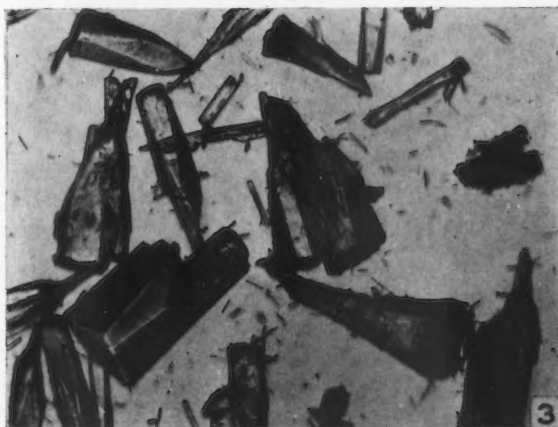
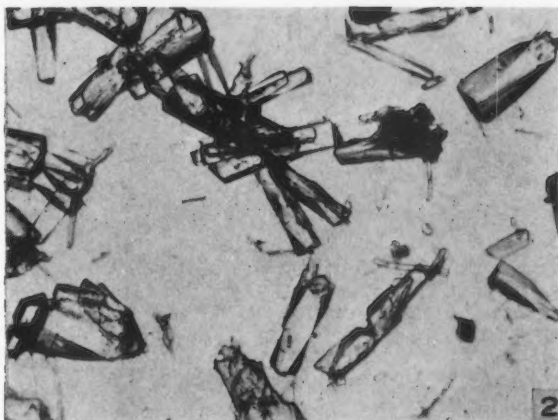


FIG. 1. *Nitroguanidine crystallized from acetone. 20 \times .*
FIG. 2. *Nitroguanidine recrystallized from ethanol. 20 \times .*
FIG. 3. *Nitroguanidine recrystallized from methanol. 20 \times .*

PLATE II



FIG. 4. *Commercial nitroguanidine.* $\times 100$.
FIG. 5. *Expt. 5 product on 60 mesh.* $\times 110$.

addition of the hot aqueous solution to the methanol gave a product having 4/5 the bulk-density of that obtained when the aqueous solution was added all at once. Since this result was not altered when the methanol was initially at 50° C. it would appear that temperature was less significant than the water-methanol ratio. Slow addition does of course impose a water-methanol ratio much higher than 1:2 at the beginning.

The experiments recorded in Table I were carried out by dissolving 600 gm. of nitroguanidine in 8000 cc. water in a paddle-stirred steam-jacketed stainless-steel vessel. This solution at 100° C. was run as rapidly as possible (four to six minutes) through a steam-jacketed delivery pipe into 16,000 cc. of methanol

TABLE I
VARIABLES IN NITROGUANIDINE CRYSTALLIZATION
To 16,000 cc. methanol were added one or more lots of 600 gm.
nitroguanidine in 8000 cc. water

Expt. No.	Time for soln. of NG, min.	Orig. temp. in kettle, ° C.	Temp. after mixing, ° C.	Time air cooling, min.	Temp. after air cooling, ° C.	Time water cooling, min.	Temp. cooling water, ° C.	Filtrate temp., ° C.	Bulk-density, loose	Bulk-density, packed	% Pptd.	Quality	Ratio
													MeOH H ₂ O
1	5	25	64	210	34	25	7	10	0.59	0.71	86	G	2
2	5	20	63	55	50	35	7	10	0.63	0.83	87	F	2
3	5	27	66	60	50	35	7	12 ¹	0.42	0.63	95	P	1
3 _a	5	12	45	110	38	80	7	10					
4	7	20	63	65	47	90	7	10	0.50	0.63	88	F	1
4 _a	20	50	50	200	36								
5	10	24	63	17	57	165	7	9	0.77	0.96	88	E	1
5 _a	10	57	69	120	48								
6	6	26	65	165	49	120	7	10	0.64	0.80	92	G	0.66
6 _a	10	60	71										
6 _b	10	66	72										
7	10	24	62	15	58	—	—		0.60	0.79	84	G	1 ²
7 _a	10	58	70	1260	24								
8	10	24	64	300	32	150	7	10	0.56	0.72	83	G	2 ²
9	10	33	65	30	61	30 30 30 30	40 25 15 7	10	0.53	0.65	91	F	1
9 _a	10	61	71	0	—								
10	10	25	63	19	57	15 120 60	38 15 7	49 ¹ 13 ¹ 10	0.55	0.70	91	F	1
10 _a	10	57	68	10	62								

¹ These are not filtration temperatures, but are the temperatures reached at the end of the cooling period and just before the second addition.

² Recovered 99% methanol was used in these experiments.

at 25° C. in a polished stainless-steel cylindrical kettle 13.5 in. in diameter by 22 in. high. The methanol was stirred by a $\frac{1}{4}$ h.p. 'Lightnin' stirrer equipped with two 3 in.-diameter three-bladed propellers turning at 1725 r.p.m. The resulting solution was then cooled with stirring to 9° to 12° C. according to the time schedules indicated in Table I.

The steam-jacketed kettle used for solution of nitroguanidine in water had a capacity of less than 2 gal., while a 12 gal. kettle was used for the crystallization operation. Since heat transfer from this latter kettle depended on cooling of the walls it was necessary to use sufficient methanol to give a 1:2 water-methanol solution after addition of the aqueous nitroguanidine solution was finished.

In order to obtain a final 1:1 water-methanol solution, the stirred slurry of crystallized nitroguanidine in the cooled 1:2 water-methanol solution was therefore treated with a second 600 gm. lot of nitroguanidine in 8000 cc. of water at 100° C. The cooling operation was then repeated as before. The quality of the crystals obtained by such duplication of the process was as good as that obtained when the final water-methanol ratio was 1:2.

These subsequent additions of hot aqueous nitroguanidine solution are shown in Table I by the letter *a*. In one case (Expt. 6b) a third aqueous nitroguanidine solution was added to the slurry. The initial and final temperatures of the slurry at the time that these additions were made are also shown in Table I.

The cooling operation was carried out in two steps. The first step was relatively slow and was accomplished simply, with our apparatus, as a spontaneous loss of heat to the air. This air-cooling was supplemented by a more rapid second step of water-cooling. This was effected by a water apron which surrounded the kettle. We found it was better to use warm water rather than cold for this operation; the use of cold water tended to cause surface crystallization on the walls of the stainless-steel kettle. This increased the proportion of fine nitroguanidine in the product.

The effect of variations in water-methanol ratio and in cooling schedule is shown in Table I by the correspondence in bulk-density (b.d.). The product was evaluated according to its loose bulk-density (weight per unit volume when poured into a 100 ml. graduated cylinder) and packed bulk-density (weight per unit volume after this same cylinder had been dropped 50 times from a height of 2.5 in. on to a leather pad).

A further classification of product is shown in Table I as Excellent, Good, Fair, and Poor. This classification is a composite one derived from two observations, which were found in most cases to correlate closely with one another. The first of these was crystal size and shape as determined by microscopic examination. Uniformity is desirable. Thus the material illustrated in Fig. 3 contains less aggregates than that shown in Fig. 2. The material shown in Fig. 3 is rated as excellent, while that shown in Fig. 2 is good, and that shown in Fig. 1 would be considered fair.

The ordinary water-crystallized nitroguanidine shown in Fig. 4 does not fit this microscopic classification in so far as its usefulness as an explosive is concerned. Thus it appears quite uniform under the microscope and it would on this basis deserve the classification 'excellent'. However, the microscopic examination does not show the actual occurrence as interlocking felted needles, because these are teased out on the microscope slide. This tendency toward 'felting' makes the material difficult to handle in bulk and it therefore deserves the classification 'poor'.

In order to supplement the microscopic examination, a pourability test was devised for inclusion in the classification, 'excellent' to 'poor', shown in Table I. Although pourability of nitroguanidine slurries in molten T.N.T. was of interest to us, we chose nitrobenzene instead, because it could be poured at a convenient temperature of 20° C. This test involved, firstly, the amount of nitrobenzene required to fill the voids (that is, to form a 'mush') and, secondly, the amount required in order that the resulting slurry would just pour from an inverted graduated cylinder after vigorous shaking.

Some classifications according to this test are shown in Table II as the number of cc. of nitrobenzene required in order that a slurry containing 2 gm. of nitroguanidine can be poured from a graduate. This evaluation conforms closely with that found by microscopic examination except in the instance, already mentioned, where interlocking of needles can occur. The dual evaluation has therefore been applied to the material obtained from the 10 experiments outlined in Table I.

TABLE II
POURABILITY OF NITROGUANIDINE SLURRIES

Type of sample	Bulk-density, packed	2 gm. nitroguanidine + cc. nitrobenzene		Qualitative classification
		To form mush	To form fluid	
Commercial nitroguanidine	0.25	4.2	>9	Very poor
Crystallization quickly from MeOH	0.37	3.4	4.3	Poor
Crystallization quickly from MeOH	0.42	2.3	3.0	Fair
Very slow crystallization, water-MeOH, 1:1	0.71	1.8	2.5	Good
Moderate crystallization, water-MeOH, 1:2	0.83	1.5	2.1	Excellent

The results in Table I show that the rate of crystallization is significant. There seems to be an optimum in the time of cooling, especially in the first step and this optimum must be close to that used in Expt. 5. This is brought out more clearly by Table III, where the screen analyses show that coarse material contributes adversely to high bulk-density. The contrast can be

TABLE III
SCREEN ANALYSES OF HIGH DENSITY NITROGUANIDINE

Twenty-five gram samples poured into 100 ml. graduate (L, loose bulk-density, b.d.) and dropped 2.5 in. for 50 times (P, packed bulk-density)

Expt. No.	Screen cuts														Over-all b.d. packed	Crystal shape							
	On 20 mesh			On 40 mesh			On 60 mesh			On 80 mesh			On 100 mesh				On 150 mesh			Pass 150 mesh			
	%	b.d.		%	b.d.		%	b.d.		%	b.d.		%	b.d.			%	b.d.		%	b.d.		
		L	P		L	P		L	P		L	P		L	P			L	P		L	P	L
1	0	0	0	7.8	.55	.69	51.2	.55	.69	17.7	.59	.72	4.9	—	—	4.4	—	—	4.0	—	—	0.71	Smooth rods.
2	0	0	0	5.8	.50	.59	51.6	.62	.72	19.1	.64	.80	8.7	—	—	9.2	—	—	5.4	—	—	0.83	Rough.
3	7.6	—	—	50.6	—	—	30.2	—	—	8.7	—	—	1.7	—	—	0.5	—	—	0.7	—	—	0.63	Non-homogeneous
4	0	—	—	15.3	.41	.56	50.4	.50	.64	17.7	.55	.69	5.0	—	—	5.0	—	—	6.6	—	—	0.63	Irregular, long.
5	0	—	—	2.9	.66	—	26.0	.70	.76	33.8	.80	.84	13.9	.84	.92	14.5	.84	.96	8.9	.66	.93	0.96	Rounded rods.
6	0	—	—	20.1	.51	.66	48.8	.62	.72	20.0	.59	.74	3.8	—	—	3.2	—	—	4.1	—	—	0.80	Irregular, long.
7	0	—	—	36.0	.62	.77	44.3	.59	.77	13.6	.55	.72	2.0	—	—	1.4	—	—	2.7	—	—	0.79	Regular.
8	0	—	—	11.8	.43	.57	61.0	.57	.72	18.5	.57	.74	2.2	—	—	2.6	—	—	3.9	—	—	0.72	Irregular.
9	0	—	—	32.7	.43	.55	39.6	.50	.66	16.5	.52	.66	2.8	—	—	3.0	—	—	5.4	—	—	0.65	Long, jagged.
10	0	—	—	25.0	.52	.64	55.4	.52	.69	14.8	.52	.69	1.0	—	—	1.2	—	—	2.6	—	—	0.70	Irregular, long.

PLATE III

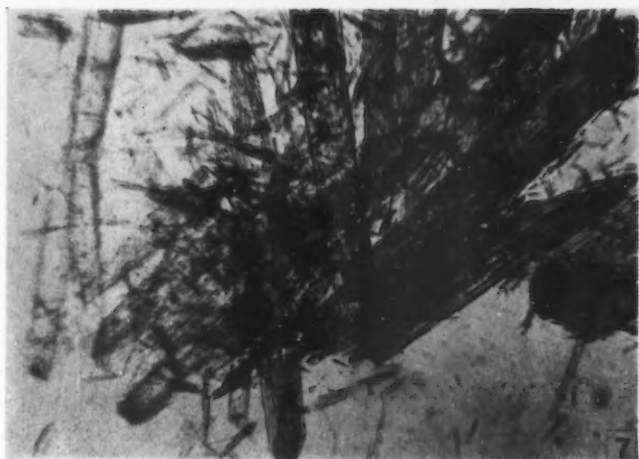
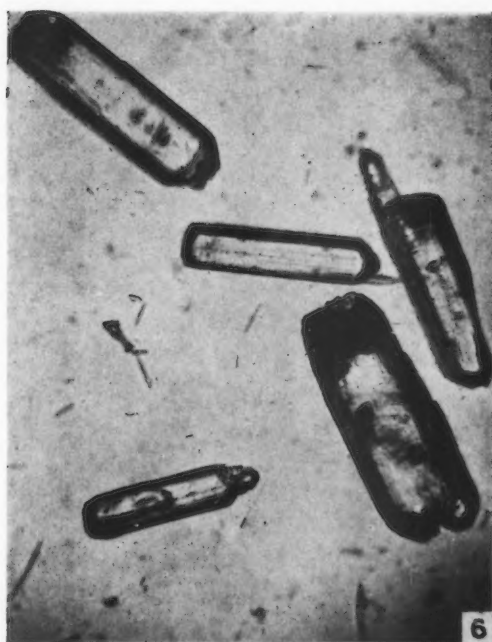
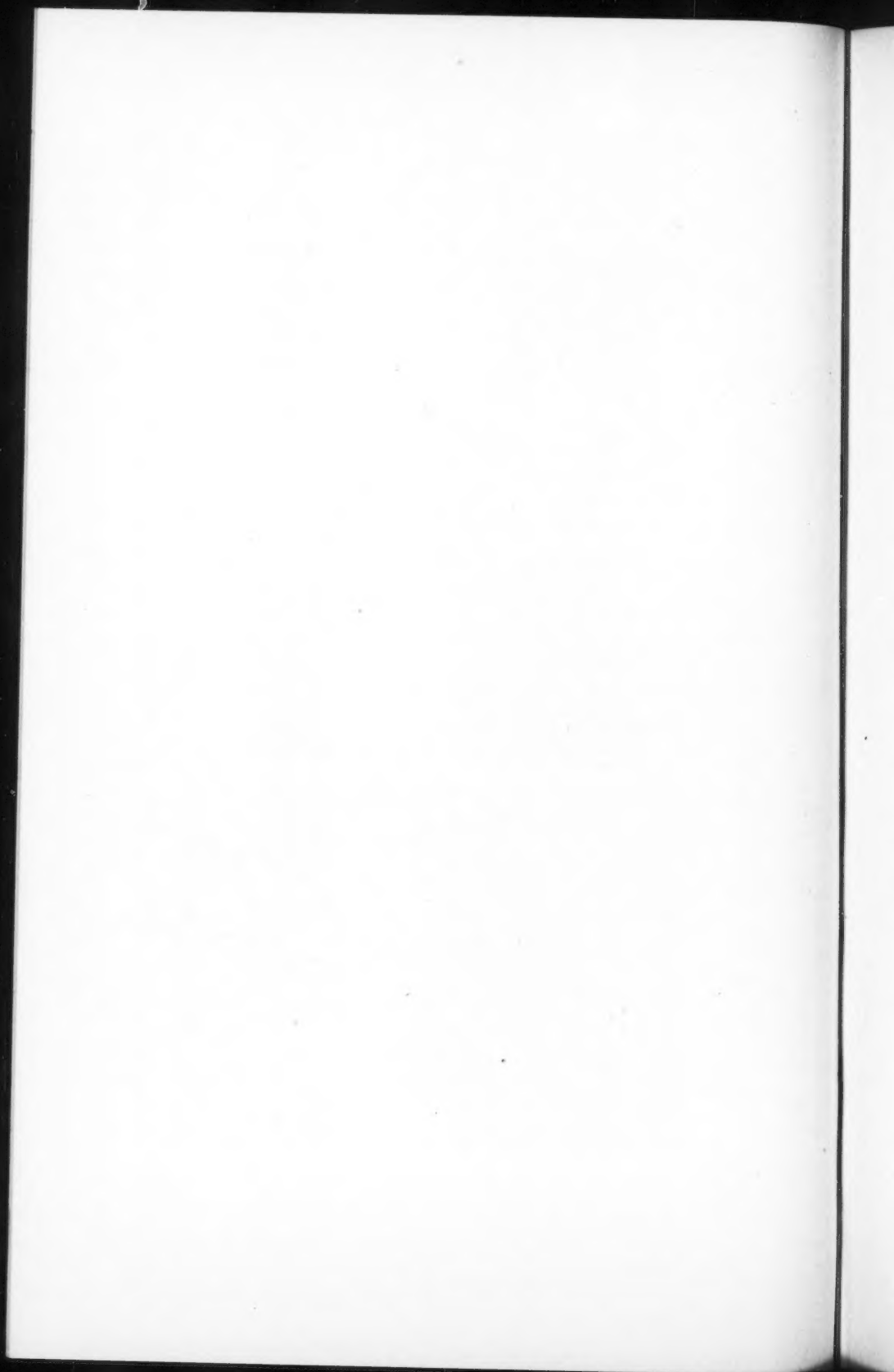


FIG. 6. *Expt. 5 product through 60 mesh.* $\times 100$.

FIG. 7. *Expt. 3 product.* $\times 110$.



made between Expt. 5 and any of Expts. 3, 7, 9, and 10. The effect of large size nitroguanidine crystals can also be demonstrated within Expt. 5 since the material through a 60 mesh screen gives a packed bulk-density of 1.0, while that retained on 60 mesh has a bulk-density of 0.67. When the latter, coarse fraction is rescreened, that retained on 60 mesh has a bulk-density of 0.85 while the material passing through 60 mesh has a bulk-density of 0.98. The effect of rescreening indicates that comminution is occurring during the operation, and this is confirmed by microscopic examination. Thus many of the coarse crystals in the material from Expt. 5 which are retained on 60 mesh show an apparent twinning such as is seen at the top in Fig. 5. That part passing through 60 mesh (Fig. 6) seems to be free from this type of twin.

The coarse screen fractions obtained from the experiments other than numbers 3 and 5 as shown in Table III also show clumped crystals such as is seen in Fig. 2. If such material is lightly ground under water, then its bulk-density and pourability are almost as good as those found for the material produced in Expt. 5. The difference is probably owing to the rounded ends of the ideal crystals shown in Fig. 6.

On the other hand, the material produced according to Expt. 3, Table I, is not materially improved by grinding. This is understandable after inspection of Fig. 7, a photomicrograph of the product. Such material is much better than commercial nitroguanidine with respect to bulk packing or pourability of slurries, but a T.N.T. slurry containing more than 30% of this material cannot be poured satisfactorily into high explosive shell. On the other hand, T.N.T. slurries containing 50% of the nitroguanidine produced according to Expt. 5 must be stirred during pouring to avoid segregation by settling of the solid phase.

In summary, a correlation of Tables I and II shows that a long cooling time for the methanol-water solution is undesirable, since it tends toward the formation of large crystal aggregates, which must be broken up by a subsequent operation. On the other hand the cooling may be too rapid, and this will lead to mixtures of crystal shapes obtained in Expt. 3. It is believed that a definite cooling schedule will have to be worked out anew for each installation, and Table I can only give a general idea of what this schedule would be. It would be advisable, therefore, to provide, in a large installation, a polished closed kettle with variable speed stirring and with provision for jacketed water-cooling over the range 65° to 10° C.

PRECISION OF LABORATORY MEASUREMENTS OF BREAKING STRENGTH OF TEXTILES¹

BY J. W. HOPKINS² AND MURIEL W. WEATHERBURN³

Abstract

Warp breaking strength was measured in five test strips from each of a series of duplicate pieces of cotton duck in rotproofing experiments. Breaks occurring at the jaws of the machine, which amounted to some 16% of the total, gave results about 3.5% lower and 20% more variable than non-jaw breaks. Discrepancies in non-jaw breaks of similarly treated fabric arose partly from variance in test strips from the same piece and partly from additional variance between duplicate pieces. Weathering tended to reduce intra-piece, and soil burial to increase both intra- and inter-piece variability. The tests as conducted were capable of discriminating differences of the order of 15 to 20%. Greater gains in precision would have resulted from increasing the number of replicate pieces than from increasing the number of strips tested per piece in the same ratio. However, determination of the most economical test procedure for specified precision in each type of material also required consideration of the cost factor, which was nearly three times as great per piece as per strip.

Introduction

When the breaking strength of a fabric is estimated in accordance with the recommendations of the American Society for Testing Materials by measuring the breaking strength of 10 or more individual test strips, it is found that owing to variations in the performance of the testing machine, in the technique of the operator, or in the cloth itself, such measurements exhibit more or less fluctuation. Statistical examination of the results may consequently be necessary to ascertain whether the average obtained for any particular fabric differs significantly from a prescribed standard or from the averages for other fabrics. If all the averages to be compared are subject to variability of about the same extent, simple and powerful tests of significance are available in the procedure due to R. A. Fisher (1, 5) widely known under the name of 'analysis of variance'. If, however, the variance of measurements on different fabrics is unequal, tests of significance must take cognizance of this fact, if incorrect conclusions are to be avoided (3).

A recent paper by Edelman (4) has shown that the variance of a lengthy series of such measurements may be far from constant. However, whereas this author was mainly concerned with the acceptance testing of a large quantity of similar material by different operators, experimenters are more likely to have to deal with measurements made by a single operator, but relating to fabric whose characteristics have been subjected to modification. It is accordingly desired to describe here some statistical features of such measurements made in these laboratories.

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Data

Data consisted of measurements of the warp breaking strength after exposure to leaching and soil burial by standard methods (2) and to outdoor weathering for four months at the National Research Laboratories, Ottawa, of unbleached cotton army duck (weight 10 oz. per sq. yd., thread count 46 three-ply warpwise and 37 two-ply weftwise per in.) treated with several series of rotproofing compounds. The experimental procedure adopted provided two random samples of fabric 6 in. warpwise by 8 in. weftwise representative of each treatment, for measurement of warp breaking strength after leaching and leaching followed by two and four weeks' soil burial, and after weathering and weathering followed by two and four weeks' soil burial. In the event, the effect of soil burial, particularly for four weeks, was so drastic as to make this determination impracticable in a number of instances; but with these exceptions five 6 by 1 in. ravelled warp strips from each 6 by 8 in. piece were broken in a motor-driven Scott D-8 tester, the initial jaw spacing being 3 in. and the rate of separation of the jaws about 12 in. per min.

Analysis

Jaw Breaks

It was reported by Edelman (4) that breaks at the jaws of the machine, comprising in his tests one-third of the whole, differed significantly in both average and variability from those occurring elsewhere along the test strip. This was attributed either to cutting action resulting from excessive tightening of the jaws, or to concentrated stresses in the fabric near the clamped portion due to uneven mounting. In an effort to minimize these adverse effects the jaws of the machine used here were coated with rubber, and this, together with care on the part of the operator, was perhaps reflected in the fact that the incidence of jaw breaks, namely 280 in 1715 or 16.3%, was only about half that noted above. These 280 jaw breaks were distributed over 354 sets of five measurements on separate pieces as follows: none in 158 (44.6%); one in 134 (37.9%); two in 43 (12.2%); three in 16 (4.5%); and four in 3 sets (0.8%). The observed numbers thus showed some approach to the calculated frequencies of 145.1, 141.6, 55.4, 10.9, 1.0, and 0.0 obtained by expansion of the binomial probability function

$$354(0.8367 + 0.1633)^5.$$

However, the actual frequency of zero and three or four significantly exceeded, while that of one or two fell short, of the random expectation for the total number of jaw breaks observed, suggesting some unevenness in the performance of the operator.

The undesirable attributes of these jaw breaks were likewise less pronounced than those reported by Edelman (4) for warp breaks of 116 W \times 56 F cotton twill. Nevertheless, they still resulted in measurements that were on the average about 3.5% lower and 20% more variable than those obtained from

the non-jaw breaks of test strips from the same pieces. Such aberrant observations occurring with variable frequency must clearly be excluded from averages that are to be compared without adjustment, and sufficient test material should accordingly be provided to make possible the required number of acceptable measurements.

Intra- and Inter-Piece Variance

Examination of the variation in breaking strength recorded for test strips from the same piece by the well-known 'control chart' method (8, 9) indicated that while this was reasonably uniform in all the pieces subjected to leaching only, it was definitely non-uniform in those undergoing weathering or soil burial.

Fig. 1 depicts the results for material leached subsequent to treatment but not otherwise modified, at which stage differences in treatment averages were of the order of 30% at most, and indicates that this series of measurements was 'in control' in the sense that it was characterized by uniform and predictable variability. The plotted points represent the range from maximum to

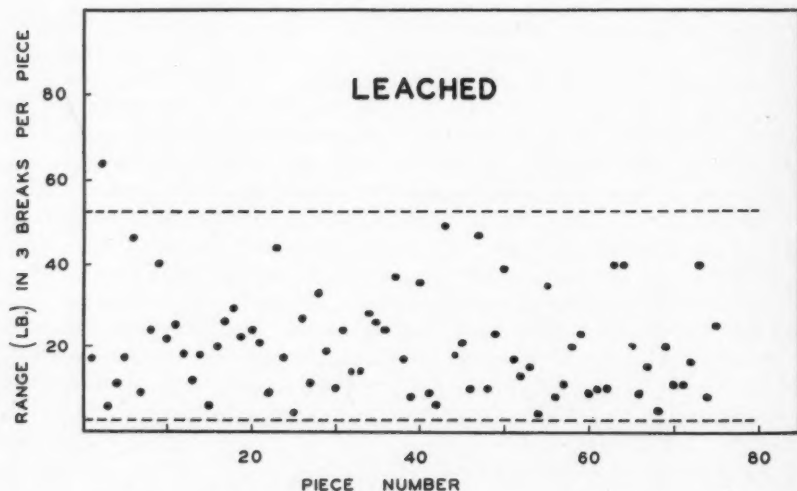


FIG. 1. Range in breaking strength of three test strips (non-jaw breaks) from each of 75 pieces subjected to leaching following rotproofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.

minimum in non-jaw breaks of three test strips from each of 75 successive pieces, while the dashed lines indicate the limits, computed from tables due to E. S. Pearson (7), outside which only one point of this number would be expected to fall if measurements on all pieces were subject to the same Gaussian error system. In Figs. 2 to 4 the range in individual measurements is shown not in chronological sequence, but in relation to the average for each

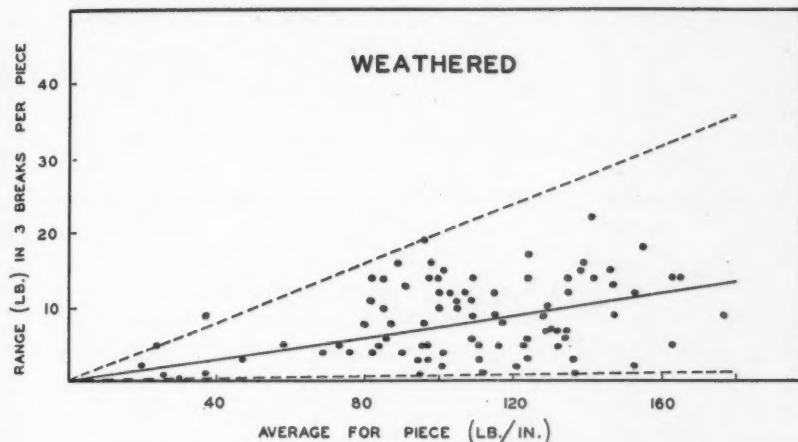


FIG. 2. Range in breaking strength of three test strips (non-jaw breaks) in relation to average strength of pieces subjected to weathering following rotproofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.

test piece, which now varied considerably. The divergence in measurements of pieces subjected to weathering only tended to increase progressively with the mean in the average ratio of 0.077 to 1, as illustrated in Fig. 2. On the other hand, after soil burial following either leaching (Fig. 3) or weathering (Fig. 4), test strips from pieces for which the average breaking force required

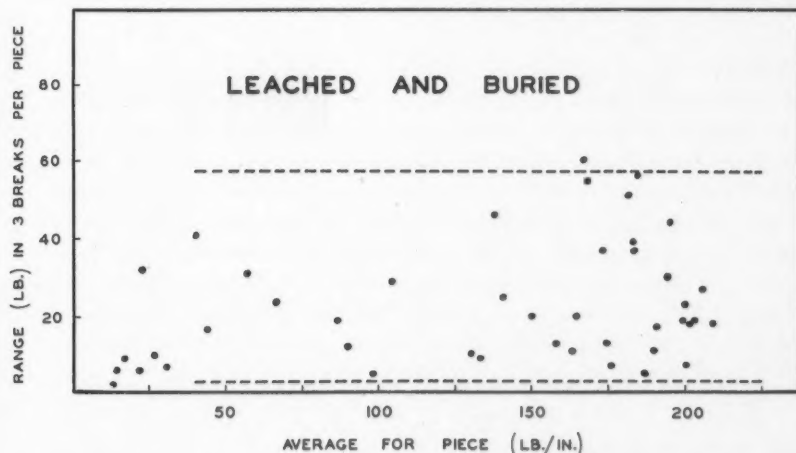


FIG. 3. Range in breaking strength of three test strips (non-jaw breaks) in relation to average strength of pieces subjected to leaching and two weeks' soil burial following rotproofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.

was less than 30 lb. gave results in much closer mutual agreement than did those from the remaining majority. The variance of these latter was, however, sensibly uniform for averages of from 30 to 200 lb. These characteristics, also observed in earlier tests, may be explicable by the consideration that whereas weathering caused a fairly uniform degradation of the entire fabric,

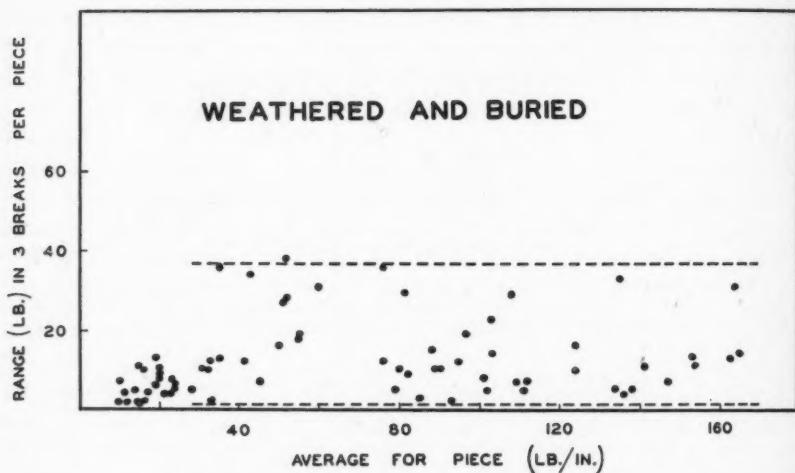


FIG. 4. Range in breaking strength of three test strips (non-jaw breaks) in relation to average strength of pieces subjected to weathering and two weeks' soil burial following rot-proofing treatment. Points represent observed ranges, dashed lines the theoretical limits within which all but one of these should fall.

soil burial resulted in more patchy damage by localized aggregates of micro-organisms. If these were distributed in accordance with Poisson's law (5), their variance would increase in proportion to their numbers, and thus might offset the reduction in variability due to general degradation of the fabric, except when the latter was so extensive as to restrict the possible range.

The inter-piece variance of the averages for duplicate pieces subjected to the same treatment and exposure was also calculable, and was found to exceed $\frac{1}{2}$ the intra-piece variance of individual test strips in the ratio of 1.6 : 1, 2.8 : 1, and 4.7 : 1 for leached, leached and buried, and weathered and buried fabric respectively (excluding all pieces whose average strength did not exceed 30 lb. per in.). Comparisons of treatment averages were therefore subject to additional uncertainty from this cause.

Tests of Statistical Significance

The precision of treatment averages was affected firstly by the rejection of unacceptable (jaw break) measurements, and secondly by the inter- and intra-piece variance of the remaining data. On the seemingly justifiable

assumption that discrepancies in the results for test strips from the same 6 by 8 in. piece originated for the most part in the experimental technique rather than in the cloth itself, the estimated variance (mean square error) of a treatment average derived from two test pieces providing n_1 and n_2 acceptable measurements was

$$\frac{1}{2}s_1^2 + \frac{1}{4} \cdot \frac{n_1 + n_2}{n_1 n_2} s_2^2$$

for an unweighted mean $\frac{1}{2}(\bar{x}_1 + \bar{x}_2)$ of the averages \bar{x}_1 and \bar{x}_2 for the two individual pieces;

$$\frac{1}{(n_1 + n_2)^2} ((n_1^2 + n_2^2) s_1^2 + (n_1 + n_2) s_2^2)$$

for a mean $(n_1 \bar{x}_1 + n_2 \bar{x}_2)/(n_1 + n_2)$ weighted in proportion to the number of acceptable measurements for each piece; and

$$\left(\frac{1}{s_1^2 + s_2^2/n_1} + \frac{1}{s_1^2 + s_2^2/n_2} \right)^{-1}$$

for a mean weighted inversely in proportion to the estimated variance $(s_1^2 + s_2^2/n_1)$ and $(s_1^2 + s_2^2/n_2)$ of the averages \bar{x}_1 and \bar{x}_2 . When $n_1 = n_2$, all three of the foregoing are equivalent. When $n_1 \neq n_2$, the third procedure gives, at the cost of some extra computation, the mean of least variance, while the first is preferable to the second if

$$s_1^2 > \frac{n_1 + n_2}{2n_1 n_2} s_2^2.$$

The values of s_1^2 and s_2^2 estimated from the data were:

	s_1^2	s_2^2
Leached	33.8	158.4
Weathered	20.6	0.002088 (mean) ²
Leached and buried 2 wk. (Average > 30 lb.)	150.7	254.2
Weathered " " " " " "	90.7	86.8

soil burial increasing the inter- and intra-piece variance of both leached and weathered material. From these, the variance of any treatment average was calculable by the formulae given in the preceding paragraph. The variance of the difference between any two averages was the sum of the variance of each, and from this the 'necessary difference' required for any specified degree of statistical significance was obtainable by taking the square root and multiplying by the appropriate probability factor (5). With five acceptable measurements on duplicate pieces for each treatment, the tests under consideration were found to be capable of discriminating differences of 17, 10, 21, and 16 lb. per in., in leached, weathered, leached and buried, and weathered and buried fabric at the 5% level of significance, the value cited for weathered material being that appropriate in the neighbourhood of the general average of 100 lb. per in.

Replication and Precision

From the foregoing estimates of s_1^2 and s_2^2 , further estimates could be made of the variance of the averages of measurements of any specified number of pieces and test strips per piece, and hence of the differences in such averages required for statistical significance. The reciprocal of the last quantity provides an index of the estimated precision attained, and the relation of this to the number of pieces and of strips per piece of leached and of weathered and buried fabric tested is illustrated in Fig. 5. In consequence of the variance

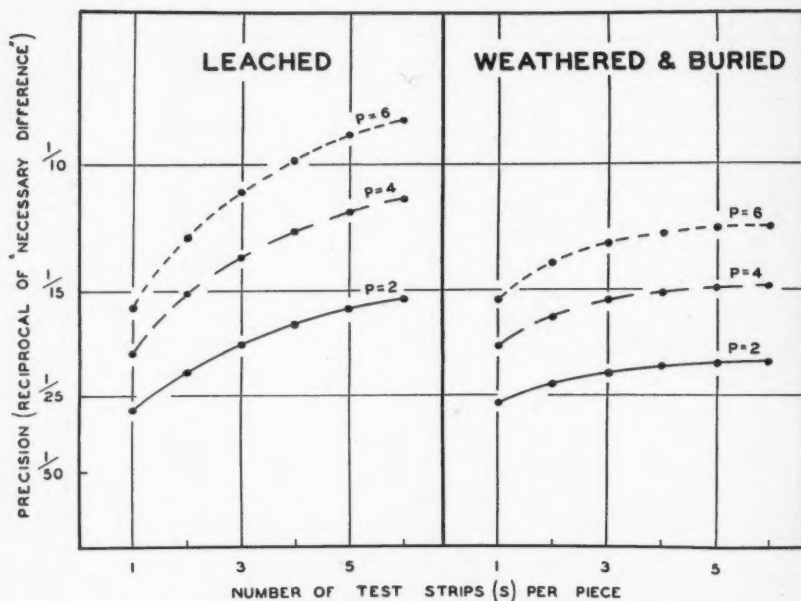


FIG. 5. Estimated precision of averages in relation to number of replicate pieces (p) and of test strips (s) per piece.

in test pieces additional to that in strips from the same piece, a greater gain in precision would have resulted from increasing the number of replicate pieces than from increasing the number of strips tested per piece in the same ratio.

This consideration (discussed elsewhere by Mandel (6) in its relation to the replication of chemical analyses) was particularly operative in the results for weathered and buried cloth, which had a large inter-piece variance, and it was estimated that the average from two test strips from each of six pieces would have been 1.7 times as precise as that from six strips (the maximum number possible) from each of two pieces of this material. However, due weight must also be given to the fact that whilst the provision of each treated and exposed 6 by 8 in. piece entailed an average expenditure of about 12 cents for materials and labour, the cost of the labour involved in preparing and

breaking a test strip averaged only about $4\frac{2}{3}$ cents. This resulted in cost in relation to the estimated precision to be obtained from different numbers of test pieces and strips varying as shown in Fig. 6. As inter-piece variance was the major source of discrepancy in measurements of weathered and buried fabric, any considerable improvement in the precision of these, if required, could be effected only by increasing the number of pieces, the devotion of labour to more than two test strips per piece being decidedly uneconomical. Moderate precision, corresponding to a 'necessary difference' of 15 or 16 lb.

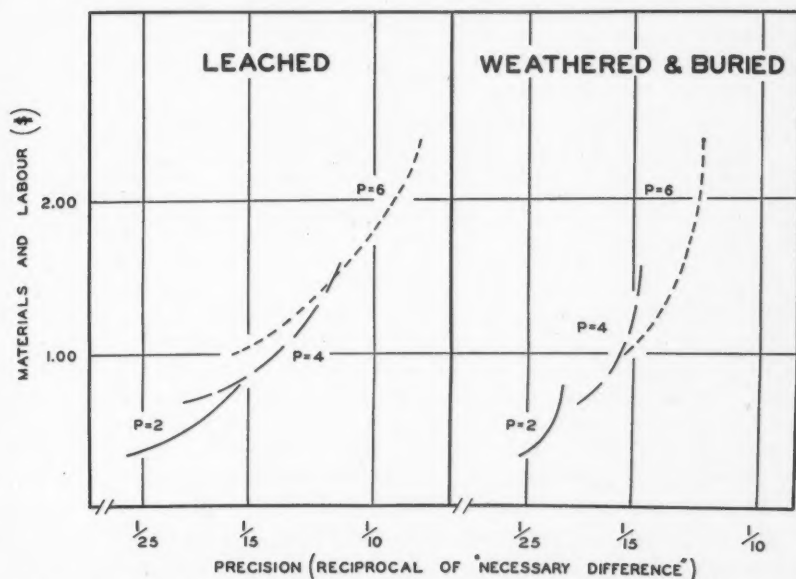


FIG. 6. Estimated cost in relation to precision of tests using two, four, and six replicate pieces (p) and one to six test strips per piece.

per in., could, however, have been obtained from either one test strip from each of six pieces or from two strips from each of four pieces subjected to leaching only. The latter would have required one-third more measurements, but in spite of this would have been 15% less costly in total materials and labour. These contrasting results emphasize the fact that quantitative study of the actual errors of measurement is prerequisite to assessment of the efficiency of test programs of this kind.

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